

## ELECTROPHOTOSENSITIVE MATERIAL

## BACKGROUND OF THE INVENTION,

The present invention relates to an electrophotosensitive material which is used in image forming apparatuses such as electrostatic copying machine, laser beam printer and facsimile and, more particularly, to an electrophotosensitive material which is excellent in durability, particularly wear resistance and gas resistance.

10 In image forming apparatuses such as electrostatic copying machine, facsimile and laser beam printer, electrophotosensitive materials having sensitivity in a wavelength range of a light source used in these image forming apparatuses are used. As the electrophotosensitive material, an inorganic photosensitive material having a photosensitive layer made of an inorganic material such as selenium and an organic photosensitive material (or organic photoconductor, OPC) having a photosensitive layer made of an organic conductive material are known. Among these photosensitive materials, the latter organic photosensitive material has widely been studied, recently, because it is easily produced as compared with the inorganic photosensitive material and has a wide range of choice of photosensitive materials such as electric charge transferring material, electric charge generating material and binder resin as well as high functional design freedom.

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To maintain quality of the formed images in a good state for a long period in the above image forming apparatuses, it is required to enhance durability of the electrophotosensitive material to an external force applied during processes of charging, 5 toner development, transfer onto papers and cleaning, and particularly to further improve wear resistance of a photosensitive layer.

In the organic photosensitive material, therefore, it has been studied to use a polycarbonate resin having high mechanical 10 strength as a binder resin for formation of the photosensitive layer (see Patent Documents 1 and 2).

As typical examples of a polyallylate, which is a polyester of diphenol, "U-polymer (R)" as a condensate of bisphenol A and phthalic acid is known. It is described that this polyallylate 15 is suited for use as a binder resin for improving the durability of the photosensitive layer because of its high heat distortion temperature and excellent mechanical properties (see Patent Document 3).

Furthermore, as a binder resin capable of forming a 20 photosensitive layer having excellent durability as compared with the "U-polymer (R)" and polycarbonate, for example, polyallylate (Patent Documents 4 and 5) wherein a diphenol component is fluorenone type bisphenol or 1,1-bis(4-hydroxyphenyl)-1-phenylethane, or polyallylate a 25 diphenol component is bisphenol C or

1,1-bis(4-hydroxyphenyl)cycloalkane and the resin has a viscosity within a predetermined range (Patent Documents 6 and 7) is disclosed.

Patent Document 1: Japanese Published Unexamined Patent  
5 Application (Kokai Tokkyo Koho Sho) No. 63-261267 (see claim 1)

Patent Document 2: Japanese Published Unexamined Patent  
Application (Kokai Tokkyo Koho Sho) No. 59-71057 (see claim 1)

Patent Document 3: Japanese Published Unexamined Patent  
Application (Kokoku Tokkyo Koho Sho) No. 61-55672 (see claim 1)

10 Patent Document 4: Japanese Published Unexamined Patent  
Application (Kokai Tokkyo Koho Hei) No. 5-297601 (see claim 1,  
Example 1 and Comparative Examples 1 to 2)

Patent Document 5: Japanese Published Unexamined Patent  
Application (Kokai Tokkyo Koho Hei) No. 5-341539 (see claim 1,  
15 Example 1 and Comparative Examples 1 to 2)

Patent Document 6: Japanese Published Unexamined Patent  
Application (Kokai Tokkyo Koho Hei) No. 9-22126 (see claim 1 and  
Comparative Example 3)

Patent Document 7: Japanese Published Unexamined Patent  
20 Application (Kokai Tokkyo Koho Hei) No. 8-110646 (see claim 1,  
paragraph [0010], paragraph [0011] and Comparative Examples 3 to  
4)

However, the effect of improving the mechanical strength  
of the photosensitive layer is insufficient at present. Even when  
25 using the binder resins described in the above publications, the

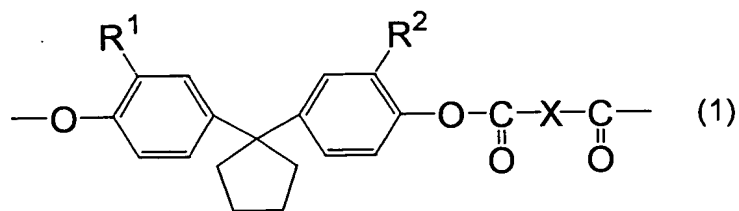
photosensitive layer causes wear within a comparatively short period when used practically in an image forming apparatus, and thus it is insufficient to achieve longer life of the electrophotosensitive material.

5           During charging of the electrophotosensitive material, an ozone gas or a NOx gas is sometimes evolved by corona discharge. Because of insufficient ozone gas or NOx gas shielding properties, a photosensitive material made of a conventional binder resin causes a problem wherein chargeability of the photosensitive  
10 material is deteriorated by exposure to the gas for a long time, namely, deterioration of charge stability during repeated exposure.

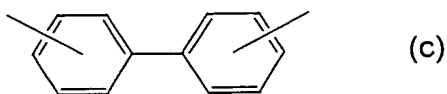
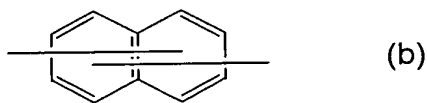
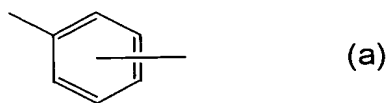
#### SUMMARY OF THE INVENTION

15           An object of the present invention is to provide an electrophotosensitive material which can achieve longer life by improving wear resistance and gas resistance while reconciling both characteristics.

          To achieve the above object, the electrophotosensitive  
20 material of the present invention is an electrophotosensitive material comprising a conductive substrate and a photosensitive layer provided on the conductive substrate, wherein the photosensitive layer contains a polyallylate having a repeating unit represented by the general formula (1):



in the formula (1), X represents any of divalent groups represented  
 5 by the formulas (a) to (c):



and  $\text{R}^1$  and  $\text{R}^2$  are the same or different and represent an alkyl  
 10 group having 1 to 3 carbon atoms.

In the electrophotosensitive material of the present  
 invention, since a polyallylate having a specific repeating unit  
 represented by the above formula is used as the binder resin for  
 formation of the photosensitive layer, the photosensitive layer  
 15 has very high wear resistance and causes less wear even when used  
 repeatedly in an image forming apparatus, and thus longer life  
 of the material can be achieved.

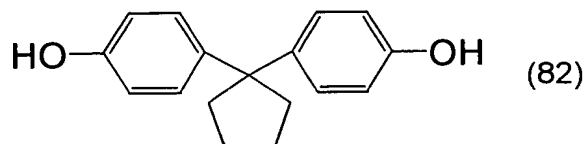
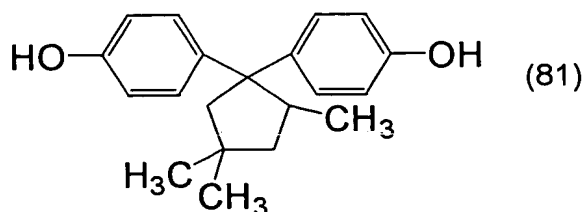
Moreover, the polyallylate having a specific repeating unit is excellent in gas resistance and is suited to achieve longer life of the electrophotosensitive material.

As described above, Patent Document 7 discloses

5 1,1-bis(4-hydroxyphenyl)cycloalkane as a dihydric phenol moiety of the polyallylate and also discloses cyclopentane as specific examples of the cycloalkane (see paragraphs [0010] and [0011]). Also the same document discloses, as a group corresponding to x in the general formula (1), phenylene group, biphenylene group  
10 and naphthylene group, similar to the case of the general formula (1) (see claim 1).

However, the document merely describes, as a specific compound (dihydric phenol moiety) in case the cycloalkane is cyclopentane,

15 1,1-bis(4-hydroxyphenyl)-3,3-dimethyl-5-methylcyclopentane [1,1-bis(4-hydroxyphenyl)-2,4,4-trimethylcyclopentane, see the following formula (81)] and 1,1-bis(4-hydroxyphenyl)cyclopentane (see the following formula (82)) (see paragraphs [0010] and [0011]).

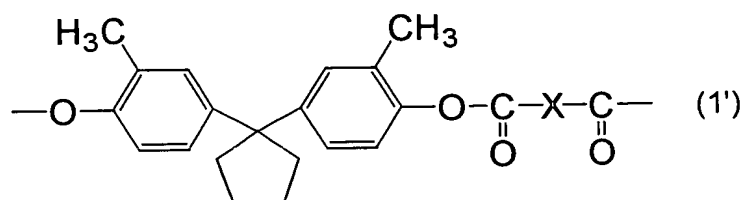


In case the dihydric phenol moiety is represented by the formula (81) or (82), namely, a group (an alkyl group having 1 to 3 carbon atoms) corresponding to  $R^1$  and  $R^2$  does not exist in the repeating unit represented by the general formula (1), as is apparent from the results of the Examples and Comparative Examples described hereinafter, it becomes difficult to form a uniform photosensitive layer because of poor solubility to a solvent for formation of the photosensitive layer.

The electrophotosensitive material of the present invention may contain the polyallylate having a repeating unit represented by the general formula (1) is in the amount of 30% by weight or more, and preferably 40% by weight or more, based on the entire binder resin for formation of the photosensitive layer.

In the electrophotosensitive material of the present invention, the substituents  $R^1$  and  $R^2$  in the repeating unit represented by the general formula (1) are preferably methyl groups. That is, the polyallylate used in the present invention

preferably has a repeating unit represented by the general formula (1').



5

As shown in the general formula (1'), in case the substituents  $R^1$  and  $R^2$  of the repeating unit (1) are alkyl groups having 1 to 3 carbon atoms, the solubility of the polyallylate having the repeating unit to the solvent used in the coating solution for formation of a photosensitive layer is improved. The smaller the bulk of the substituents  $R^1$  and  $R^2$  (namely, the smaller the number of carbon atoms of the alkyl group), the more, gas resistance and wear resistance of the photosensitive material can be further improved.

15

The electrophotosensitive material of the present invention preferably comprises:

(I) an electrophotosensitive material comprising a photosensitive layer of a single layer, said layer containing a polyallylate having a repeating unit represented by the general formula (1) and at least an electric charge generating material and an electric charge transferring material, or

20

(II) an electrophotosensitive material comprising a



photosensitive layer of a laminate composed of two or more layers,  
a layer containing a polyallylate having a repeating unit  
represented by the general formula (1) among two or more layers  
being an outermost layer of the photosensitive layer and also being  
5 a layer containing no electric charge generating material.

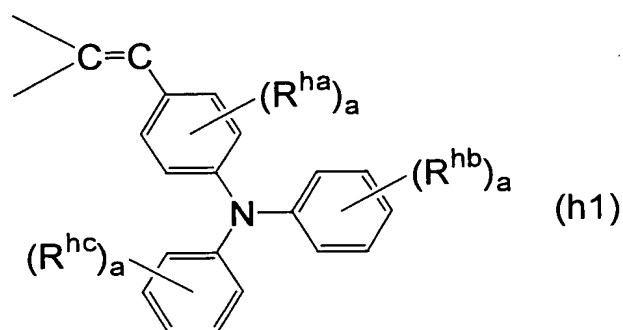
Both of the electrophotosensitive materials (I) and (II)  
are preferable aspects of the present invention and the  
electrophotosensitive material (I) is a single-layer type  
electrophotosensitive material, while the electrophotosensitive  
10 material (II) is a multi-layer type electrophotosensitive  
material.

Since the polyallylate having a repeating unit represented  
by the general formula (1) used as the binder resin in the  
electrophotosensitive material of the present invention has a  
15 feature capable of improving durability of the photosensitive  
layer, particularly wear resistance and gas resistance, the above  
polyallylate may be used as the binder resin of the layer present  
on the surface side of the photosensitive material (outer layer)  
in the multi-layer type photosensitive material. The binder resin  
20 in the inner layer of the photosensitive material may be replaced  
by the other binder resin or a binder resin whose content is increased  
when blended with the polyallylate, taking account of matching  
or solubility with the electric charge generating material or the  
electric charge generating material.

25 In the electrophotosensitive material of the present

invention, the photosensitive layer contains the polyallylate having a repeating unit represented by the general formula (1) and a hole transferring material and the hole transferring material has a triphenylaminostyryl group represented by the general formula

5 (h1):



in the formula (h1),  $R^{ha}$  to  $R^{hc}$  are the same or different and represent  
 10 an alkyl group having 1 to 8 carbon atoms, an alkoxy group having 1 to 8 carbon atoms, or an aryl group having 12 or less carbon atoms and, in case two or more of the substituents  $R^{ha}$  to  $R^{hc}$  are substituted on the same benzene ring, the substituents  $R^{ha}$  to  $R^{hc}$  substituted on adjacent carbon atoms may be combined with each  
 15 other to form a saturated or unsaturated hydrocarbon ring, and  $a$  represents an integer of 0 to 3, in the molecule.

Since the hole transferring material is particularly excellent in matching with the polyallylate having a repeating unit represented by the general formula (1), it is more preferably  
 20 to use the both in combination so as to improve the sensitivity

of the electrophotosensitive material.

#### DETAILED DESCRIPTION OF THE INVENTION

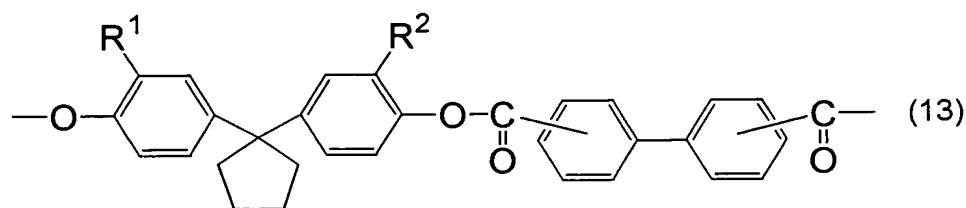
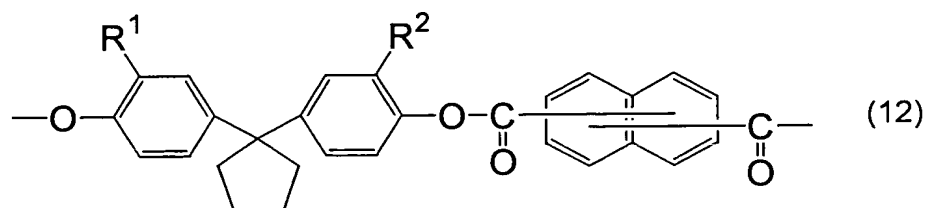
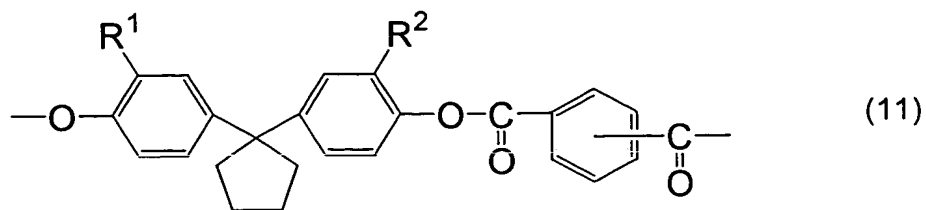
The electrophotosensitive material of the present invention  
5 will be described in detail below.

[Binder resin]

As described above, the binder resin used in the  
electrophotosensitive material of the present invention contains  
a polyallylate having a repeating unit represented by the general  
10 formula (1). The content of the polyallylate is 30% by weight  
or more, and preferably 40% by weight or more, based on the entire  
binder resin for formation of the photosensitive layer.

A viscosity-average molecular weight [Mv] of the  
polyallylate having the repeating unit (1) is preferably from 5,000  
15 to 200,000, and more preferably from 15,000 to 100,000, in terms  
of bisphenol A type polycarbonate.

Specifically, the repeating unit (1) is represented by any  
one of the general formulas (11) to (13):



in the formulas (11) to (13),  $R^1$  and  $R^2$  are as defined above.

As described above,  $R^1$  and  $R^2$  of the repeating units (11)  
 5 to (13) are more preferably methyl groups.

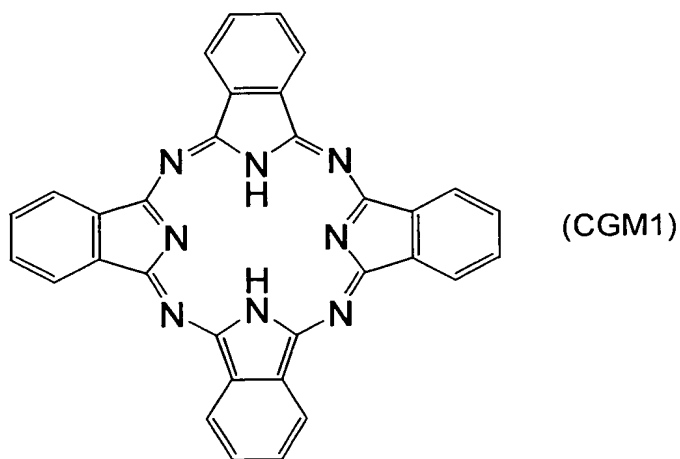
The polyallylate having the repeating unit is excellent in  
 compatibility between the electric charge generating material and  
 the electric charge transferring material and does not contain  
 a portion, which adversely affects electric charge transferrability  
 10 of the electric charge transferring material, in the molecule.  
 Therefore, when electrophotosensitive material contains the  
 polyallylate as the binder resin, there can be exerted the effect  
 of achieving longer life by improving wear resistance and gas  
 resistance of the electrophotosensitive material while  
 15 reconciling both characteristics.

In the electrophotosensitive material of the present

invention, as the binder resin, the above polyallylate having the repeating unit may be used in combination with at least one resin selected from the group consisting of polycarbonate, polyester, polyallylate having the other repeating unit of the general formula (1), polystyrene and polymethacrylate ester.

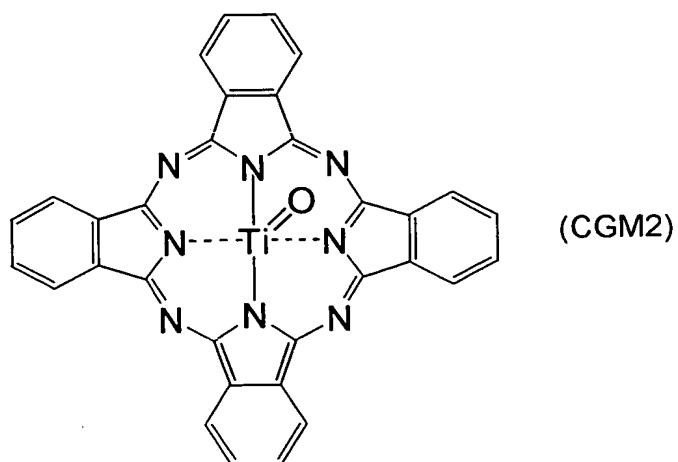
[Electric charge generating material]

Examples of the electric charge generating material, which can be used in the electrophotosensitive material of the present invention, include conventionally known various electric charge generating materials, for example, phthalocyanine pigments such as metal-free phthalocyanine ( $H_2Pc$ ) represented by the formula (CGM1):

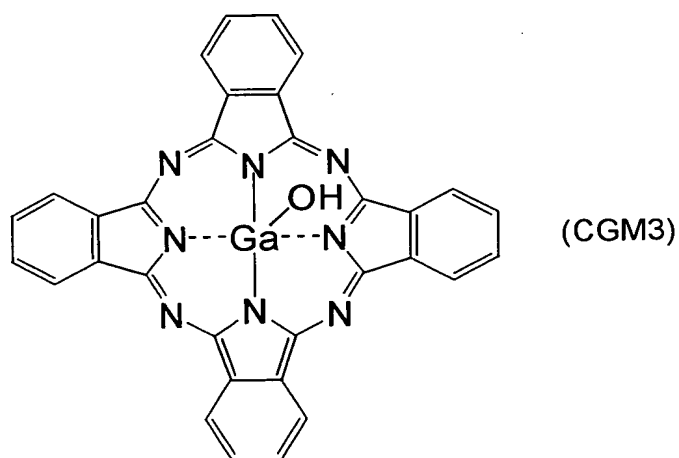


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, titanylphthalocyanine ( $TiOPc$ ) represented by the formula (CGM2):

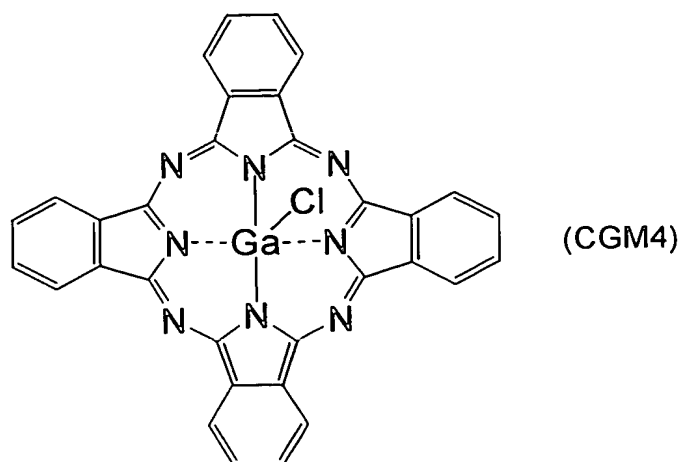


, hydroxygalliumphthalocyanine represented by the formula (CGM3):



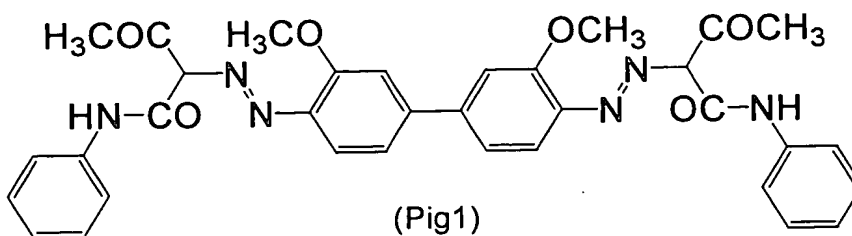
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and chlorogalliumphthalocyanine represented by the formula (CGM4):



; disazo pigments, disazo condensed pigments, monoazo pigments, perylenepigments, dithioketopyrrolopyrrolepigments, metal-free  
 5 naphthalocyanine pigments, metallic naphthalocyanine pigments, squaline pigments, trisazo pigments, indigo pigments, azulenium pigments, cyanine pigments, pyrylium salts, anthanthrone pigments, triphenylmethane pigments, threne pigments, toluidine pigments, pyrrazoline pigments, and quinacridone pigments.

10 To improve characteristics such as dispersibility in the binder resin of the electric charge generating material, the electrophotosensitive material may contain azo pigments such as C.I. Pigment Orange 16 represented by the formula (Fig 1):



The electric charge generating material may be selected from those described above so that the electrophotosensitive material has sensitivity in the desired absorption wavelength range. These electric charge generating materials may be used alone, or two or more kinds of them may be used in combination.

Digital optical image forming apparatus, for example, laser beam printer using a semiconductor laser and facsimile require a photosensitive material having sensitivity within a wavelength range of 600 nm or higher among the above electric charge generating materials. Therefore, phthalocyanine pigments such as metal-free phthalocyanine (CGM1) and titanyl phthalocyanine (CGM2) are preferably used.

The crystal form of the phthalocyanine pigments is not specifically limited and phthalocyanine pigments having various crystal forms can be used. As the metal-free phthalocyanine (CGM1), those having X type or I type crystal form are used. As the titanyl phthalocyanine (CGM2), those having  $\alpha$  type [having principal diffraction peaks at Bragg angle ( $2\theta \pm 0.2^\circ$ ) of  $7.6^\circ$  and  $28.6^\circ$  in an X-ray diffraction spectrum] or Y type [having a principal diffraction peak at Bragg angle ( $2\theta \pm 0.2^\circ$ ) of  $27.2^\circ$  in an X-ray diffraction spectrum] crystal form are used. As the hydroxygalliumphthalocyanine (CGM3), those having V type crystal form are used. As the chlorogalliumphthalocyanine (CGM4), those having II type crystal form are used. The phthalocyanine pigments having these crystal form are preferable in order to further improve



the sensitivity of the photosensitive material.

In analog optical image forming apparatuses, for example, electrostatic copying machine using a white light source such as halogen lamp, perylene and bisazo pigments having sensitivity in  
5 a visible range are preferably used among the above electric charge generating materials.

[Electric charge transferring material]

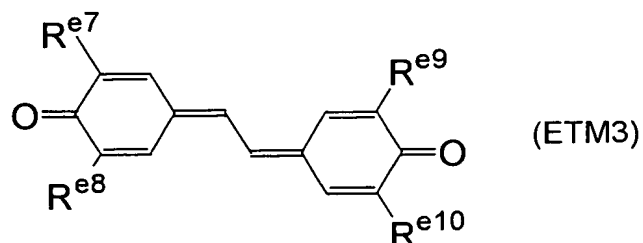
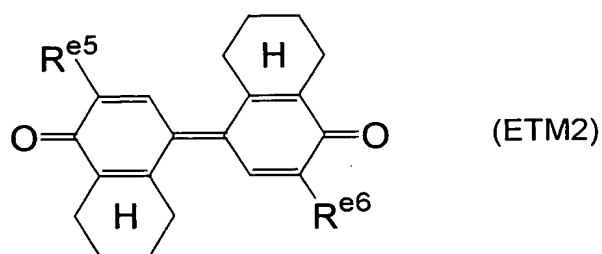
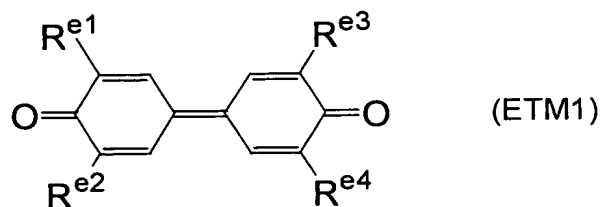
Examples of the electric charge transferring material used in the electrophotosensitive material of the present invention  
10 include conventionally known electron transferring materials and/or hole transferring materials.

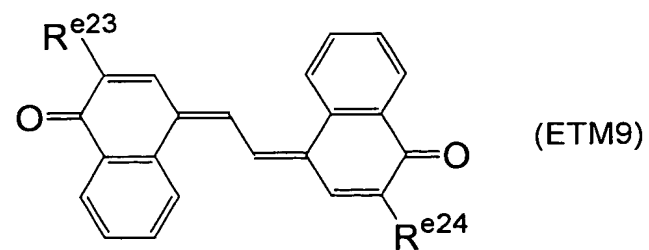
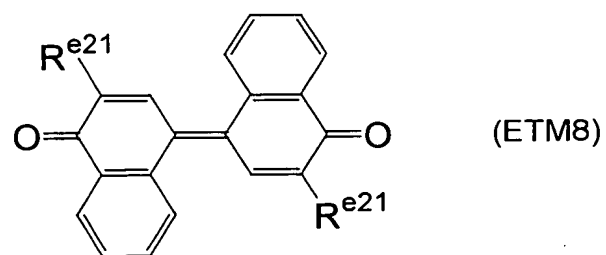
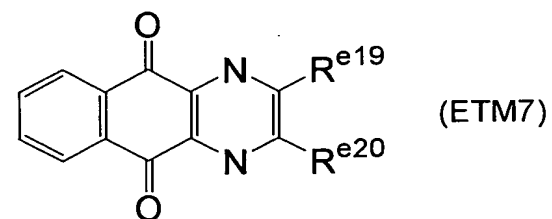
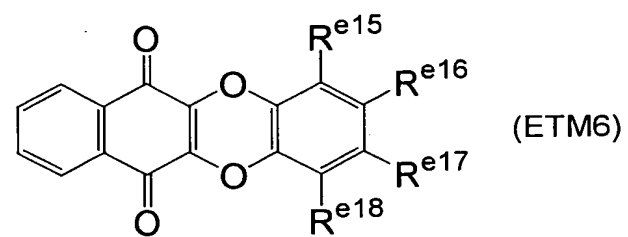
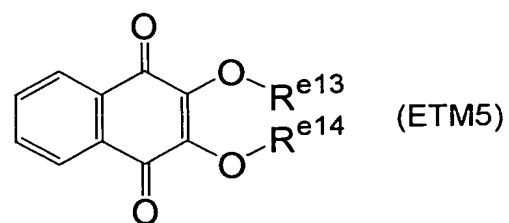
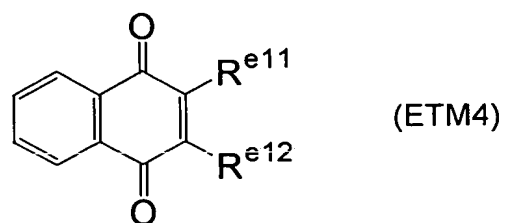
Selection of the use or either (or both) of the electron transferring material and the hole transferring material may be decided according to the layer structure and charge polarity of  
15 the photosensitive material. In a single-layer type electrophotosensitive material, if a charge transfer complex is not produced between the electron transferring material and the hole transferring material, a mixture of both materials is preferably incorporated into the photosensitive layer.

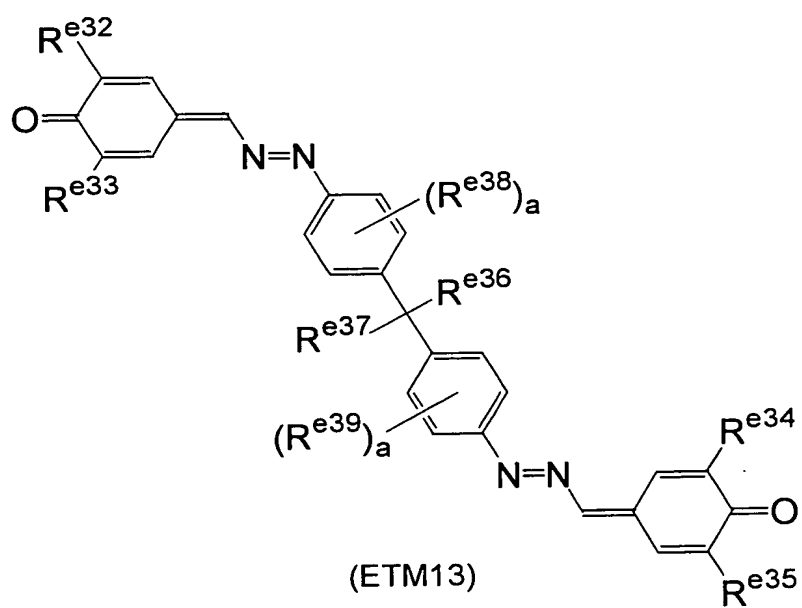
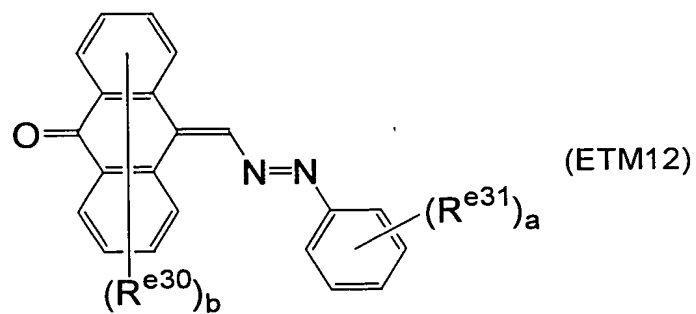
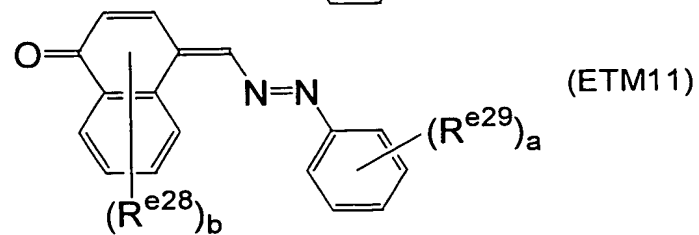
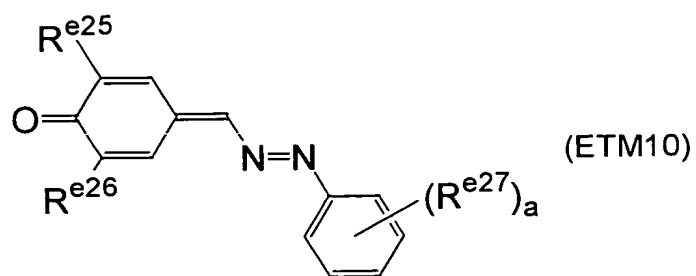
20 (Electron transferring material)

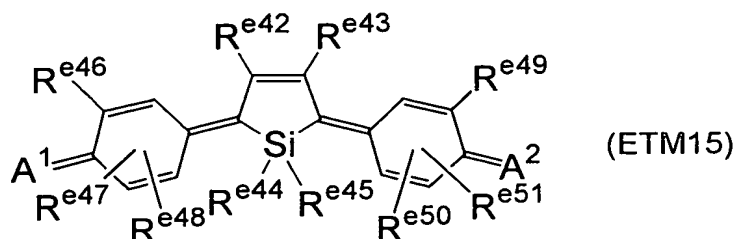
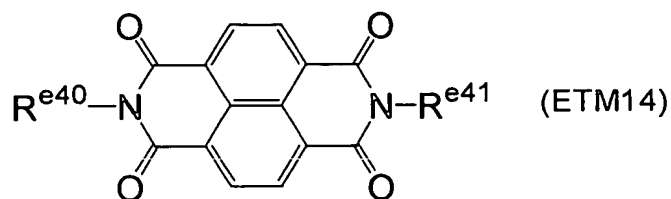
Examples of the electron transferring material, which can be used in the electrophotosensitive material of the present invention, include conventionally known various electron transferring materials. Among these electron transferring  
25 materials, diphenoquinone derivatives represented by the following

general formulas (ETM1) and (ETM2), a stilbenequinone derivative represented by the following general formula (ETM3), naphthoquinone derivatives represented by the following general formulas (ETM4), (ETM5), (ETM6) and (ETM7), dinaphthoquinone derivatives represented by the following general formulas (ETM8) and (ETM9), azoquinone derivatives represented by the following general formulas (ETM10), (ETM11), (ETM12) and (ETM13), a dimide naphthalenetetracarboxylate derivative represented by the following general formulas (ETM14), and silacyclopentadiene derivatives represented by the following general formulas (ET15) are preferable.









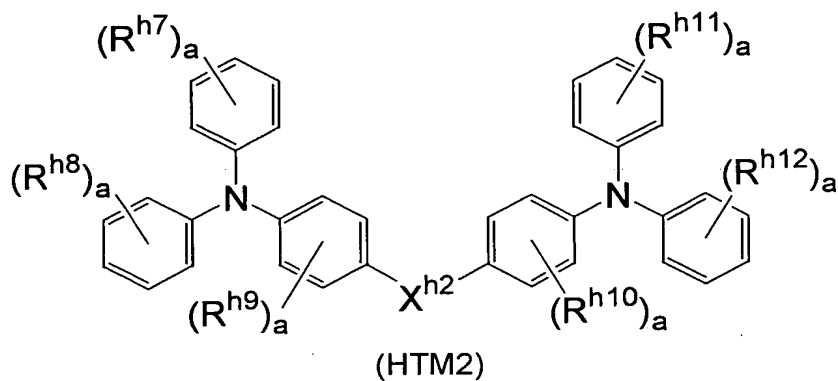
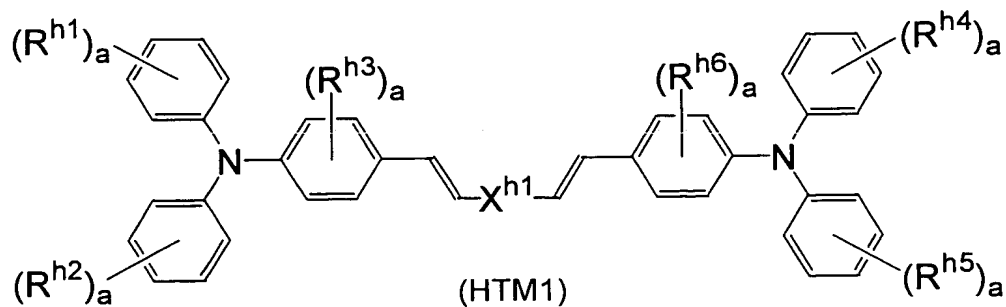
5            In the formulas (ETM1) to (ETM15),  $R^{e1}$  to  $R^{e11}$ ,  $R^{e13}$  to  $R^{e26}$ ,  
 $R^{e32}$  to  $R^{e37}$ ,  $R^{e40}$  and  $R^{e41}$  are the same or different and represent  
 a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, or  
 an aryl group having 12 or less carbon atoms.  $R^{e12}$  represents a  
 hydrogen atom, an alkyl group having 1 to 8 carbon atoms, an aryl  
 10 group having 12 or less carbon atoms, an alkylcarbonyl group having  
 1 to 9 carbon atoms, an alkoxycarbonyl group having 1 to 9 carbon  
 atoms, an arylcarbonyl group having 13 or less carbon atoms, or  
 an aryloxycarbonyl group having 13 or less carbon atoms.  $R^{e27}$ ,  
 $R^{e29}$  and  $R^{e31}$  are the same or different and represent an alkyl group  
 15 having 1 to 8 carbon atoms, an aryl group having 12 or less carbon  
 atoms, a chlorine atom, or a nitro group.  $R^{e28}$ ,  $R^{e30}$ ,  $R^{e38}$  and  $R^{e39}$   
 are the same or different and represent an alkyl group having 1  
 to 8 carbon atoms or an aryl group having 12 or less carbon atoms.  
 $A^1$  and  $A^2$  are the same or different and represent  $=O$ ,  $=C(COOR^{11})_2$   
 20 or  $=C(CN)_2$ .  $R^{e42}$  to  $R^{e51}$  are the same or different and represent

a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, an alkoxy group having 1 to 8 carbon atoms, a fluoroalkyl group having 1 to 8 carbon atoms, or an aryl group having 12 or less carbon atoms.  $R^{e52}$  represents an alkyl group having 1 to 8 carbon atoms or a fluoroalkyl group having 1 to 8 carbon atoms. a represents an integer of 0 to 3 and b represents an integer of 0 to 4.

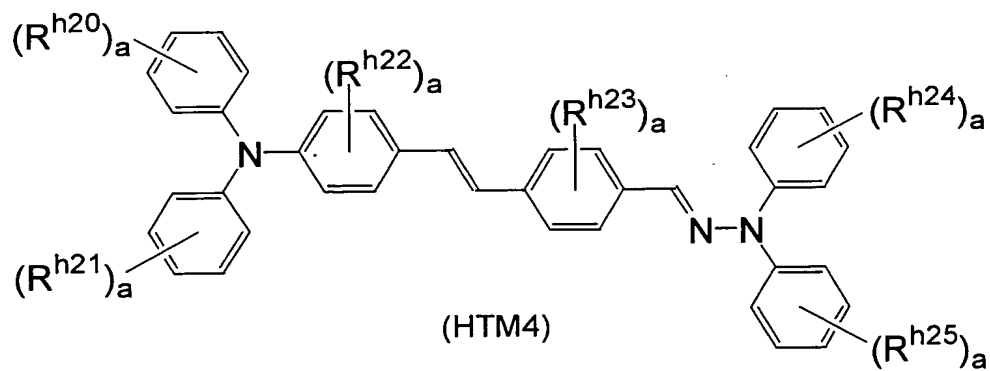
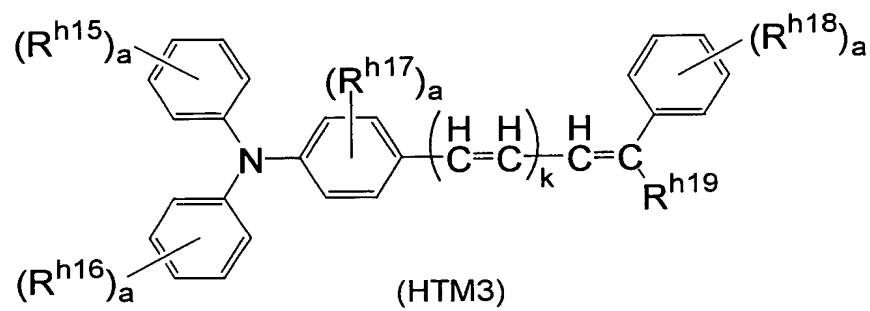
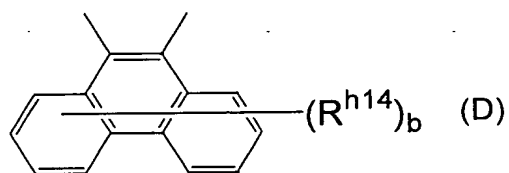
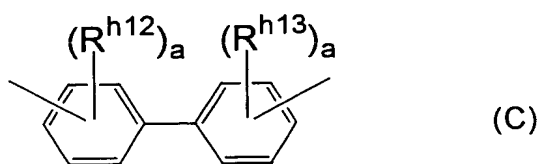
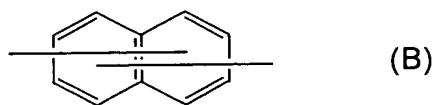
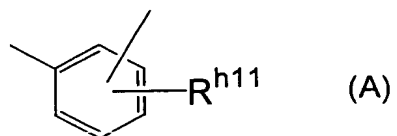
These electron transferring materials may be used alone, or two or more kinds of them may be used in combination.

(Hole transferring material)

10        Examples of the hole transferring material, which can be used in the electrophotosensitive material of the present invention, include conventionally known various hole transferring materials. Among these hole transferring materials, a bisstilbenediamine derivative represented by the following  
 15        general formula (HTM1), a bistriphenylamine derivative represented by the following general formula (HTM2), a triphenylaminostyryl derivative represented by the following general formula (HTM3), and a stilbeneamine-hydrazone derivative represented by the following general formula (HTM4) are preferably  
 20        used.



$X^{h1}$  of the formula (HTM1) represents any of the following  
 formulas (A) to (C) and  $X^{h2}$  of the formula (HTM2) represents any  
 5 of the following formulas (A) to (D).





In the formula (HTM1) to (HTM4),  $R^{h1}$  to  $R^{h18}$  and  $R^{h20}$  to  $R^{h25}$  are the same or different and represent an alkyl group having 1 to 8 carbon atoms, an alkoxy group having 1 to 8 carbon atoms, or an aryl group having 12 or less carbon atoms.  $R^{h19}$  represents  
 5 hydrogen atom, an alkyl group having 1 to 8 carbon atoms, or an aryl group having 12 or less carbon atoms. a and b are as defined above. k represents an integer of 0 to 3.

These hole transferring materials are characterized in that they have particularly high electric charge transferrability and  
 10 are less likely to form a charge transfer complex between the hole transferring material and the electron transferring material, and are also excellent in compatibility with a binder resin such as polyallylate having a repeating unit represented by the general formula (1).

15 Among these hole transferring materials, those having a triphenylaminostyryl group represented by the formula (h1) in the molecule (those represented by the general formulas (HTM1), (HTM3) and (HTM4)) are more preferable.

These hole transferring materials may be used alone, or two  
 20 or more kinds of them may be used in combination.

[Dispersion medium]

In the electrophotosensitive material of the present invention, examples of a dispersion medium used to prepare a coating solution by dispersing and dissolving the respective components  
 25 such as electric charge generating material, electric charge

transferring material and binder resin therein include various organic solvents which have conventionally been used as a solvent of a coating solution for formation of a photosensitive layer. Examples of the organic solvent include alcohols such as methanol, ethanol, isopropanol, and butanol; aliphatic hydrocarbons such as n-hexane, octane, and cyclohexane; aromatic hydrocarbons such as benzene, toluene, and xylene; halogenated hydrocarbons such as dichloromethane, dichloroethane, chloroform, carbon tetrachloride, and chlorobenzene; ethers such as dimethyl ether, diethyl ether, tetrahydrofuran, dioxane, dioxolane, ethylene glycol dimethyl ether, and diethylene glycol dimethyl ether; ketones such as acetone, methyl ethyl ketone, and cyclohexanone; esters such as ethyl acetate and methyl acetate; and dimethylformaldehyde, dimethylformamide and dimethyl sulfoxide.

In the present invention, among these organic solvents, at least one organic solvent selected from the group consisting of tetrahydrofuran, dioxane, dioxolane, cyclohexanone, toluene, xylene, dichloromethane, dichloroethane and chlorobenzene is preferably used in order to stably disperse the respective components such as electric charge generating material, electric charge transferring material and binder resin, but is not specifically limited.

[Other components]

In addition to the respective components described above, conventionally known various additives such as oxidation

inhibitors, radical scavengers, singlet quenchers, antioxidants (e.g. ultraviolet absorbers), softeners, plasticizers, surface modifiers, excipients, thickeners, dispersion stabilizers, waxes, acceptors and donors can be incorporated into the coating solution for formation of a photosensitive layer as far as electrophotographic characteristics are not adversely affected. For the purpose of improving the sensitivity of the photosensitive layer, known sensitizers such as terphenyl, halonaphthoquinones and acenaphthylene may be used in combination with the electric charge generating material. To improve the dispersibility of the electric charge transferring material and electric charge generating material and the smoothness of the surface of the photosensitive layer, surfactants and leveling agents may be added. [Conductive substrate]

As the conductive substrate on which the photosensitive layer is formed, for example, various materials having the conductivity can be used. The substrate includes, for example, conductive substrates made of metallic simple substances such as iron, aluminum, copper, tin, platinum, silver, vanadium, molybdenum, chromium, cadmium, titanium, nickel, palladium, indium, stainless steel and brass; substrates made of plastic materials prepared by depositing or laminating the above metals; substrates made of glasses coated with aluminum iodide, tin oxide and indium oxide; and resin substrates containing fine conductive particles such as carbon black particles dispersed therein.

The conductive substrate may be in the form of a sheet or drum according to the structure of the image forming apparatus to be used. The substrate itself may have the conductivity, or the surface of the substrate may have the conductivity. The  
5 conductive substrate may be preferably those having a sufficient mechanical strength during service.

[Process for producing electrophotosensitive material]

The method of forming a photosensitive layer in the electrophotosensitive material of the present invention differs  
10 according to the case of a so-called single-layer type photosensitive material wherein an electric charge generating material and an electric charge transferring material are incorporated in the same layer, and a multi-layer type  
photosensitive material wherein a layer containing an electric  
15 charge generating material (electric charge generating layer) and a layer containing an electric charge transferring material (electric charge transferring layer) are separated. Any  
photosensitive layer is formed by dissolving and dispersing a binder resin containing a polyallylate having a repeating unit  
20 represented by the general formula (1) and components for formation of the photosensitive layer, for example, electric charge  
generating material and electric charge transferring material in a solvent, applying the resulting coating solution on a conductive  
substrate (directly or via an under coat layer) and drying the  
25 coating solution.

(Process for producing single-layer type electrophotosensitive material)

The single-layer type electrophotosensitive material is obtained by dispersing or dissolving an electric charge generating material, an electron transferring material, a binder resin and, if necessary, a hole transferring material and other components in a proper dispersion medium, applying the resulting coating solution for formation of a photosensitive layer on a conductive substrate, and drying the coating solution to form a photosensitive layer.

In the coating solution for formation of the photosensitive layer, the electric charge generating material may be incorporated in the amount within a range from 0.1 to 50 parts by weight, and preferably from 0.5 to 30 parts by weight, based on 100 parts by weight of the binder resin. The electron transferring material may be incorporated in the amount within a range from 5 to 200 parts by weight, and preferably from 10 to 100 parts by weight, based on 100 parts by weight of the binder resin. The electron transferring material other than the silacyclopentadiene derivative (1) of the present invention may be incorporated as far as the effect of the present invention is not adversely affected. The hole transferring material may be incorporated in the amount within a range from 5 to 500 parts by weight, and preferably from 25 to 200 parts by weight, based on 100 parts by weight of the binder resin. When using the electron transferring material in

combination with hole transferring material, the total amount of the electron transferring material and the hole transferring material is usually controlled within a range from 20 to 500 parts by weight, and preferably from 30 to 200 parts by weight, based on 100 parts by weight of the binder resin.

The thickness of the photosensitive layer formed by applying the coating solution for formation of a photosensitive layer is preferably controlled within a range from 5 to 100  $\mu\text{m}$ , and particularly preferably from 10 to 50  $\mu\text{m}$ .

10 In case of forming the photosensitive layer by the coating method, the electric charge generating material, the electric charge transferring material, the insoluble azo pigment, the binder resin and the proper solvent are dispersed and mixed using a known means such as roll mill, ball mill, attritor, paint shaker, or  
15 ultrasonic dispersing apparatus to prepare a dispersion, and then the resulting dispersion is applied by using a known means and then dried.

(Process for producing multi-layer type electrophotosensitive material)

20 In the production of a multi-layer type electrophotosensitive material, first, an electric charge generating material, a binder resin and, if necessary, other components are dispersed or dissolved in a proper solvent, and then the coating solution for formation of an electric charge  
25 generating layer is applied on a conductive substrate and dried

to form an electric charge generating layer. Then, an electric charge transferring material (at least one of an electron transferring material and a hole transferring material), a binder resin and, if necessary, other components are dispersed or  
5 dissolved in a proper solvent and the resulting coating solution for formation of an electric charge transferring layer is applied on the electric charge generating layer and then dried to form an electric charge transferring layer. Thus, an electrophotosensitive material comprising a conductive substrate  
10 and an electric charge generating layer and an electric charge transferring layer laminated on the conductive substrate in this order can be obtained.

The order of lamination of the electric charge generating layer and the electric charge transferring layer may be reverse  
15 to the above order. Since the electric charge generating layer has a small thickness and is insufficient in strength, the electric charge generating layer and the electric charge transferring layer are preferably laminated in this order.

Although it is not specifically limited in single-layer type  
20 and multi-layer type electrophotosensitive materials of the present invention, an under coat layer (barrier layer) may be formed between the conductive substrate and the photosensitive layer as far as the characteristics of the photosensitive material are not adversely affected. Also a protective layer may be formed on the  
25 surface of the photosensitive material.

## EXAMPLES

The following Examples and Comparative Examples further illustrate the present invention in detail.

## 5 [Synthesis of polyallylate]

## Synthesis Example 1

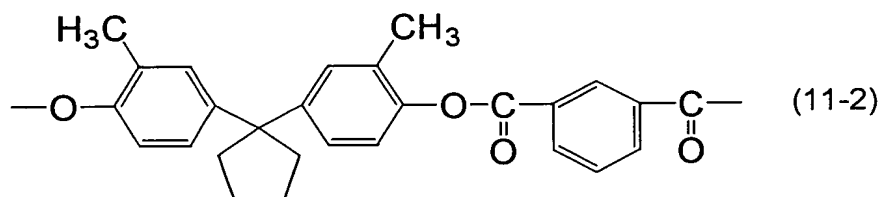
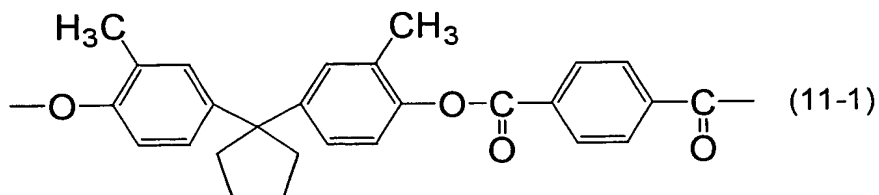
56.4 g (0.20 mol) of  
1,1-bis(3-methyl-4-hydroxyphenyl)cyclopentane, 1.5 g (0.010 mol)  
of tert-butyl phenol and 16.0 g (0.40 mol) of sodium hydroxide  
10 were dissolved in 1.1 L of water and trimethylbenzylammonium  
chloride as a polymerization catalyst was added to the aqueous  
alkali solution thus obtained, followed by vigorous stirring. The  
amount of the polymerization catalyst was adjusted to 0.5 mol%  
based on 1,1-bis(3-methyl-4-hydroxyphenyl)cyclopentane.

15 20.2 g (0.10 mol) of terephthaloyl chloride and 20.2 g (0.10  
mol) of isophthaloyl chloride were dissolved in 0.73 L of  
dichloromethane and the dichloromethane solution thus obtained  
was added to the above aqueous alkali solution while stirring,  
and thus the polymerization reaction was initiated. The  
20 polymerization reaction was carried out for 3 hours and the  
temperature of the reaction solution during the reaction was  
adjusted to 20°C. After 3 hours, acetic acid was added in the  
reaction system, thereby to terminate the polymerization reaction.

After the completion of the polymerization reaction, the  
25 reaction solution was washed with water and then slowly added in



methanol while stirring after confirming that the aqueous layer is neutralized. The precipitate was collected by filtration and then dried to obtain 72 g of a polyallylate (resin-1) having a repeating unit represented by the following formula (11-1) and  
 5 a repeating unit represented by the following formula (11-2) in a molar ratio of 1:1.



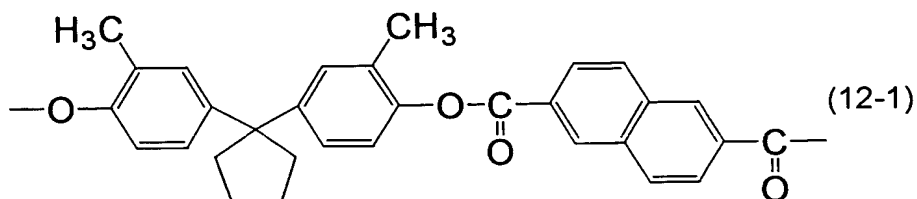
10 An inherent viscosity  $\eta_{inh}$  of the resulting polyallylate (resin-1) was measured by a tetrachloroethane solvent. As a result, it was 0.645.

#### Synthesis Example 2

15 In the same manner as in Synthesis Example 1, except that 15.1 g (0.06 mol) of 2,6-naphthalenedicarbonyl dichloride and 28.3 g (0.14 mol) of isophthaloyl chloride were used in place of terephthaloyl chloride and isophthaloyl chloride, a polyallylate was synthesized.

The resulting polyallylate has a repeating unit represented

by the following formula (12-1) and a repeating unit represented by the above formula (11-2) in a molar ratio of 3:7.



5

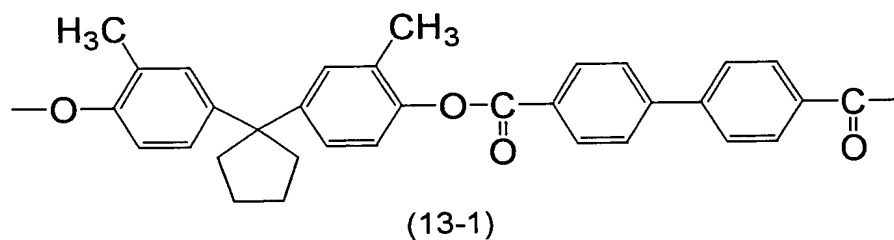
The inherent viscosity  $\eta_{inh}$ . (solvent: tetrachloroethane) of the resulting polyallylate (resin-2) was 0.72.

#### Synthesis Example 3

In the same manner as in Synthesis Example 1, except that  
 10 55.6 g (0.20 mol) of 4,4'-biphenyldicarbonyl dichloride was used in place of terephthaloyl chloride and isophthaloyl chloride, a polyallylate was synthesized.

The resulting polyallylate has a repeating unit represented by the following formula (13-1).

15

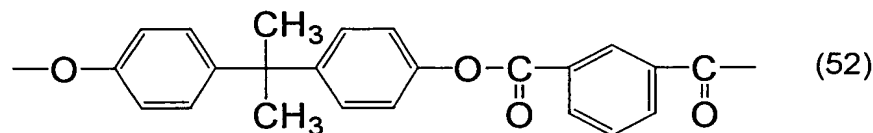
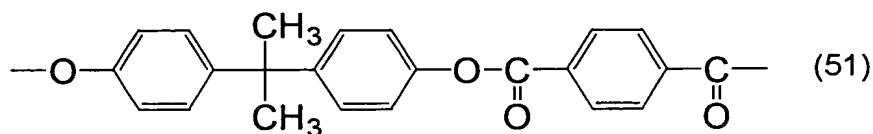


The inherent viscosity  $\eta_{inh}$ . (solvent: tetrachloroethane) of the resulting polyallylate (resin-3) was 0.650.

## Comparative Synthesis Example 1

In the same manner as in Synthesis Example 1, except that 45.6 g (0.20 mol) of 2,2-bis(4-hydroxyphenyl)propane was used in place of 1,1-bis(3-methyl-4-hydroxyphenyl)cyclopentane, a  
 5 polyallylate was synthesized.

The resulting polyallylate has a repeating unit represented by the following formula (51) and a repeating unit represented by the following formula (52) in a molar ratio of 1:1.



10

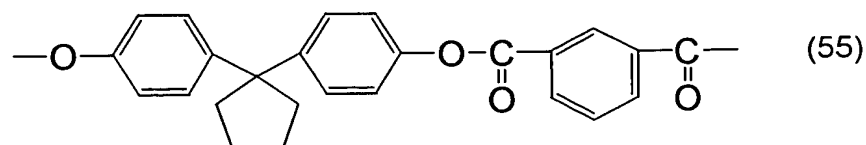
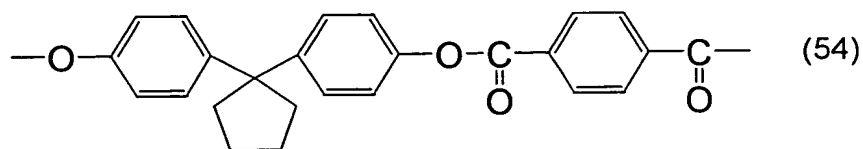
The inherent viscosity  $\eta_{inh}$ . (solvent: tetrachloroethane) of the resulting polyallylate (resin-4) was 0.721.

## Comparative Synthesis Example 2

15 In the same manner as in Synthesis Example 1, except that 50.8 g (0.20 mol) of 1,1-bis(4-hydroxyphenyl)cyclopentane was used in place of 1,1-bis(3-methyl-4-hydroxyphenyl)cyclopentane, a polyallylate was synthesized.

The resulting polyallylate has a repeating unit represented  
 20 by the following formula (54) and a repeating unit represented

by the following formula (55) in a molar ratio of 1:1.



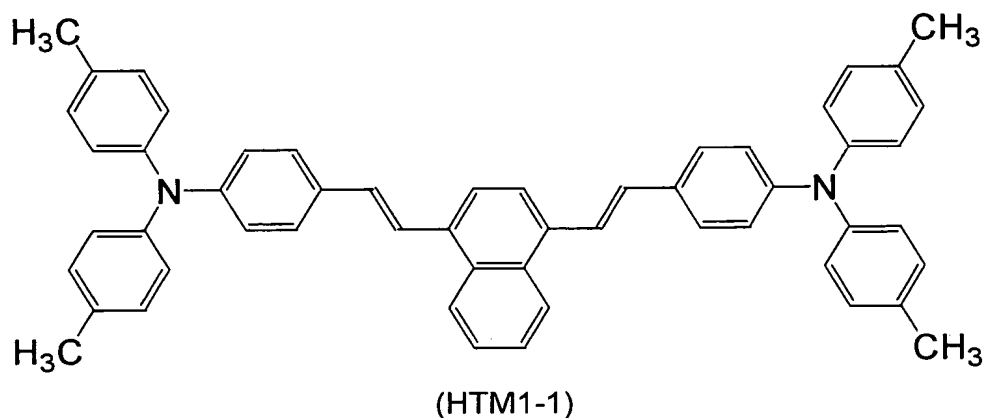
- 5           The inherent viscosity  $\eta_{inh}$ . (solvent: tetrachloroethane)  
of the resulting polyallylate (resin-6) was 0.705.

[Production of electrophotosensitive material]

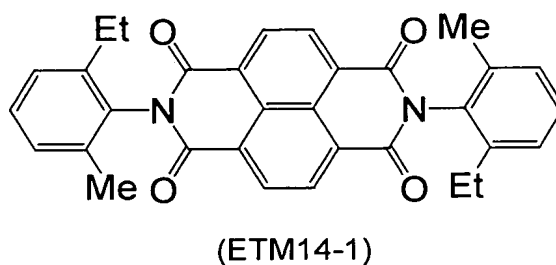
#### Example 1

- 3.5 Parts by weight of an X type metal-free phthalocyanine  
10 (X-H<sub>2</sub> Pc) as the electric charge generating material, 50 parts  
by weight of a bisstilbenediamine derivative represented by the  
following formula (HTM1-1) as the hole transferring material, 30  
parts by weight of a diphenoquinone derivative represented by the  
following formula (ETM14-1) as the electron transferring material,  
15 0.1 parts by weight of a leveling agent [dimethylsilicone oil,  
manufactured by SHIN-ETSU CHEMICAL CO., LTD. under the trade name  
of "KF-96-50CS"] and 100 parts by weight of the binder resin  
(polyallylate (resin-1)) obtained in Synthesis Example 1 were added  
in 600 parts by weight of a solvent (tetrahydrofuran) and then  
20 dissolved and dispersed using an ultrasonic disperser to obtain

a coating solution for formation of a single-layer type photosensitive layer.



5



in the formula (ETM14-1), Me represents a methyl group and Et represents an ethyl group.

10        The above electric charge generating material is a metal-free phthalocyanine represented by the formula (CGM1), which has an X type crystal form.

15        Then, the above coating solution is applied on an aluminum substrate using a silicone blade and dried at 110°C for 40 minutes to obtain an electrophotosensitive material having a 35 μm thick single-layer type photosensitive layer.

## Examples 2 and 3

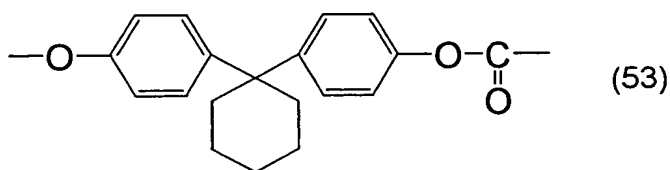
In the same manner as in Example 1, except that the polyallylate (resin-2) obtained in Synthesis Example 2 was used as the binder resin in place of the polyallylate (resin-1) obtained in Synthesis Example 1 in Example 2 and that the polyallylate (resin-3) obtained in Synthesis Example 3 was used in place of the polyallylate (resin-1) obtained in Synthesis Example 1 in Example 3, single-layer type electrophotosensitive materials were produced.

## 10 Comparative Example 1

In the same manner as in Example 1, except that the polyallylate (resin-4) obtained in Comparative Synthesis Example 1 was used as the binder resin in place of the polyallylate (resin-1) obtained in Synthesis Example 1, a single-layer type electrophotosensitive material was produced.

## Comparative Example 2

In the same manner as in Example 1, except that a polycarbonate (resin-5) having a repeating unit represented by the following formula (53) was used as the binder resin in place of the polyallylate (resin-1) obtained in Synthesis Example 1, a single-layer type electrophotosensitive material was produced.



As the polycarbonate (resin-5), a polycarbonate manufactured by Mitsubishi Engineering-Plastics Corporation under the trade name of "Iupilon (R) Z-300" (viscosity-average molecular weight [Mv]: 32,000) was used.

5 (Evaluation of physical properties)

With respect to the single-layer type electrophotosensitive materials of Examples 1 to 3 and Comparative Examples 1 to 2, the following tests for evaluation of physical properties (1) and (2) were carried out.

10 (1) Measurement of sensitivity upon positive charging

An electrophotosensitive material was mounted to an electrostatic copying machine [manufactured by KYOCERA MITA CORPORATION under the trade name of "KM-5530"] and, after charging the surface at +800 V and exposing the surface to red semiconductor  
15 laser light having a wavelength of 780 nm, a surface potential (bright potential) was measured.

The value of the surface potential upon exposure may be +160 V or lower.

(2) Measurement of wear amount

20 After measuring the thickness of a photosensitive layer of an electrophotosensitive material, a continuous copying test of 100,000 sheets was carried out in the same manner as in a conventional copying operation, except that the electrophotosensitive material was mounted to a digital copying machine [aforementioned "KM-5530"]  
25 and paper feeding and delivering was not carried out.

After the completion of continuous printing, the electrophotosensitive material was removed from a photosensitive material drum and the thickness of the photosensitive layer was measured, and then a change in thickness before and after subjecting to continuous printing (wear amount) was calculated.

The wear amount may be 1.2  $\mu\text{m}$  or less.

The results of the evaluation of physical properties with respect to Examples 1 to 3 and Comparative Examples 1 to 2 are shown in Table 1.

10 [Table 1]

[Single-layer type photosensitive material]

CGM: CGM1, HTM: HTM1-1, ETM: ETM14-1

	Binder resin	Evaluation of physical properties	
		Sensitivity upon positive charging (V)	Wear amount ( $\mu\text{m}$ )
Example 1	Resin-1	136	1.09
Example 2	Resin-2	130	1.01
Example 3	Resin-3	130	1.02
Comparative Example 1	Resin-4	127	1.52
Comparative Example 2	Resin-5	127	1.29

As is apparent from Table 1, the electrophotosensitive materials of both Examples and Comparative Examples were excellent in sensitivity. With respect to the durability (wear resistance) of the photosensitive layer, the electrophotosensitive materials of the Comparative Examples exhibit large wear amount, while the

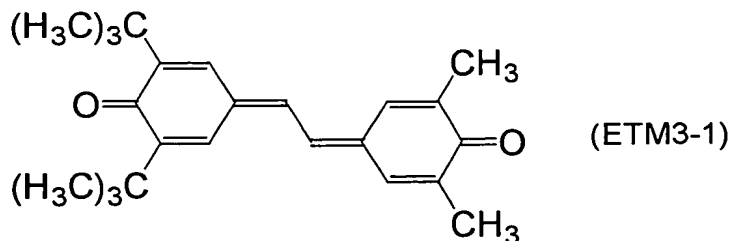
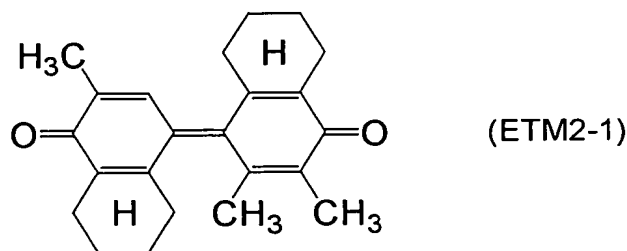
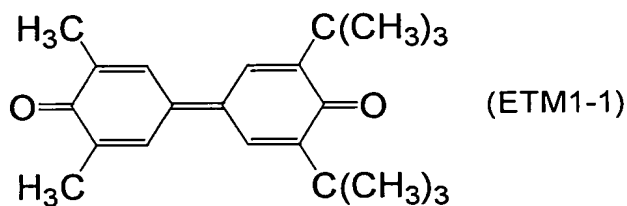


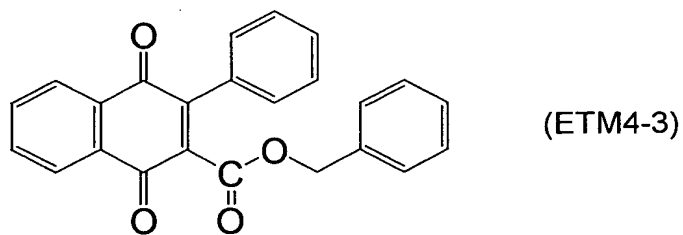
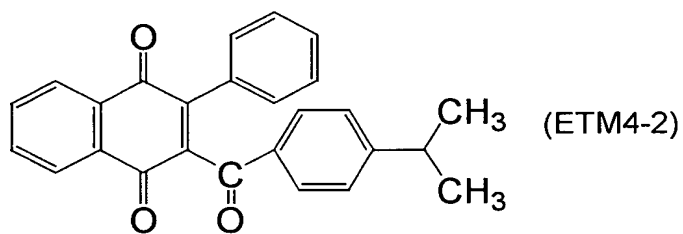
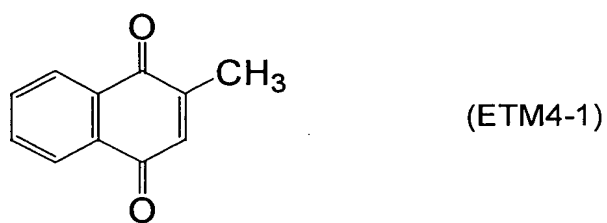
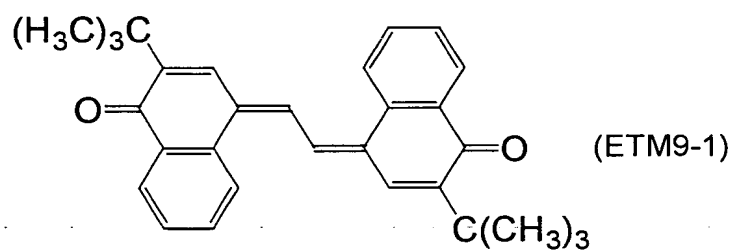
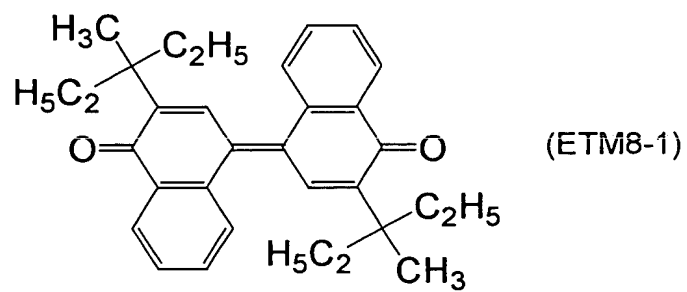
electrophotosensitive materials of the Examples exhibit very small wear amount. Therefore, a difference in wear resistance between them was noticeable.

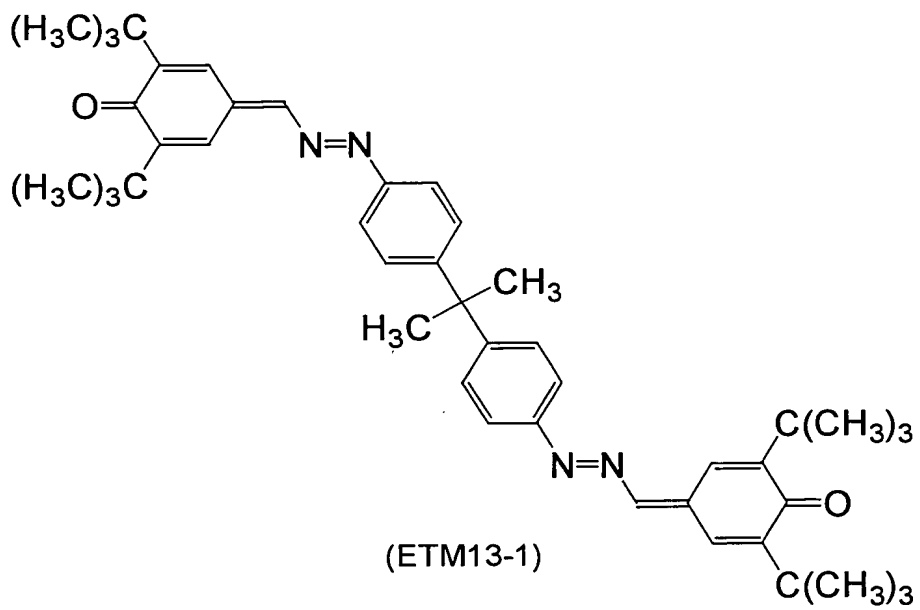
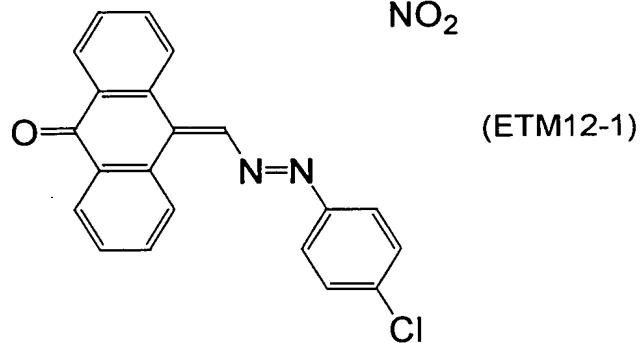
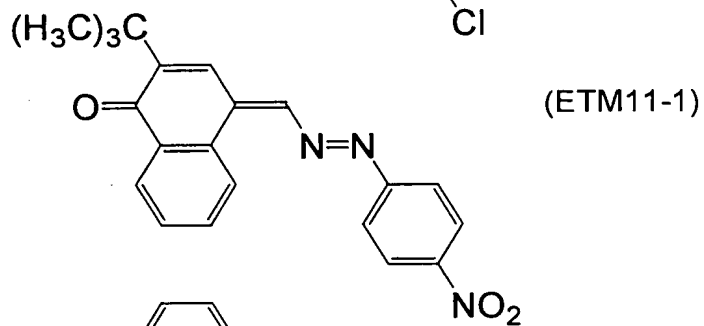
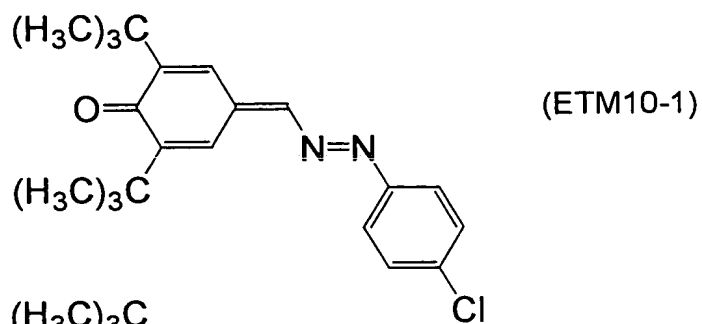
Examples 4 to 16

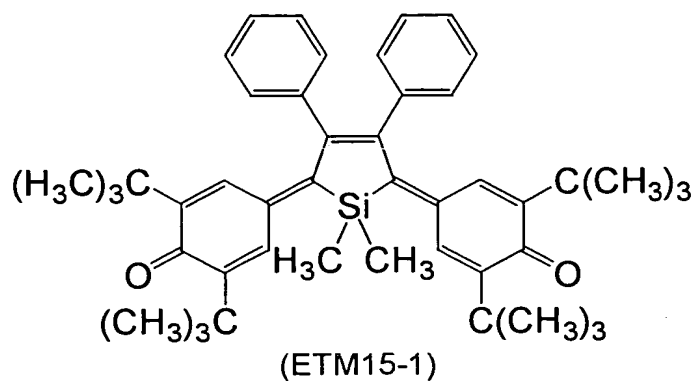
- 5 In the same manner as in Example 1, except that compounds shown in Table 2 were used as the electron transferring material in place of the compound represented by the formula (ETM14-1), single-layer type electrophotosensitive materials were produced.

The electron transferring materials shown in Table 2 are  
10 as follows.









With respect to the single-layer type electrophotosensitive materials of Examples 4 to 16, the evaluation of physical properties  
5 (measurement of sensitivity upon positive charging and wear amount) was carried out in the same manner as in Example 1. The results are shown in Table 2.

[Table 2]

[Single-layer type photosensitive material]

CGM: CGM1, HTM: HTM1-1

	Photosensitive layer-forming material		Evaluation of physical properties	
	Binder resin	ETM	Sensitivity upon positive charging (V)	Wear amount ( $\mu\text{m}$ )
Example 1	Resin-1	ETM14-1	136	1.09
Example 4	Resin-1	ETM1-1	146	1.01
Example 5	Resin-1	ETM2-1	140	1.09
Example 6	Resin-1	ETM3-1	130	1.02
Example 7	Resin-1	ETM8-1	129	1.05
Example 8	Resin-1	ETM9-1	128	1.11
Example 9	Resin-1	ETM4-1	155	1.11
Example 10	Resin-1	ETM4-2	144	1.14
Example 11	Resin-1	ETM4-3	142	1.09
Example 12	Resin-1	ETM10-1	136	1.00
Example 13	Resin-1	ETM11-1	136	1.00
Example 14	Resin-1	ETM12-1	132	1.04
Example 15	Resin-1	ETM13-1	145	1.13
Example 16	Resin-1	ETM15-1	132	1.07

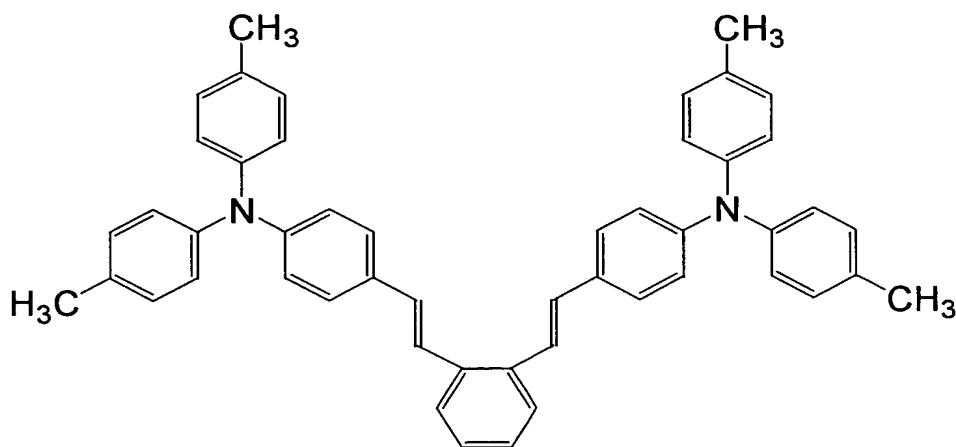
As is apparent from Table 2, the electrophotosensitive materials of all Examples were excellent in sensitivity and durability (wear resistance).

Examples 17 to 22 and Comparative Example 3 to 6

In Examples 17 to 22, single-layer type electrophotosensitive materials were produced in the same manner as in Example 1, except that compounds shown in Table 3 were used as the hole transferring material in place of the compound represented by the formula (HTM1-1).

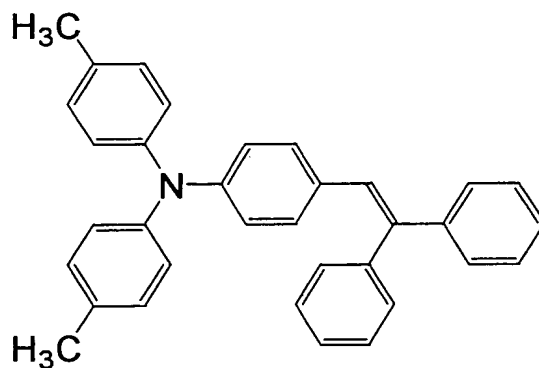
In Comparative Example 3 to 6, single-layer type electrophotosensitive materials were produced in the same manner as in Example 1, except that a compound represented by the following formula (HTM5-2) or (HTM5-3) was used as the hole transferring material and the polyallylate (resin-4) or the polyallylate (resin-5) was used as the binder resin.

The hole transferring materials shown in Table 3 are as follows.

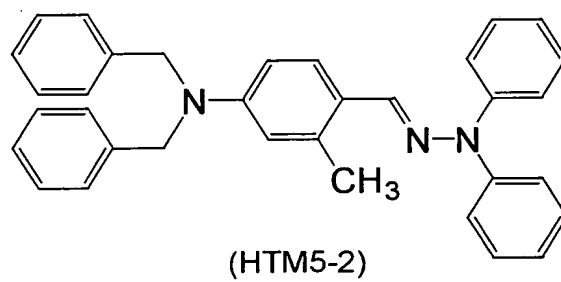
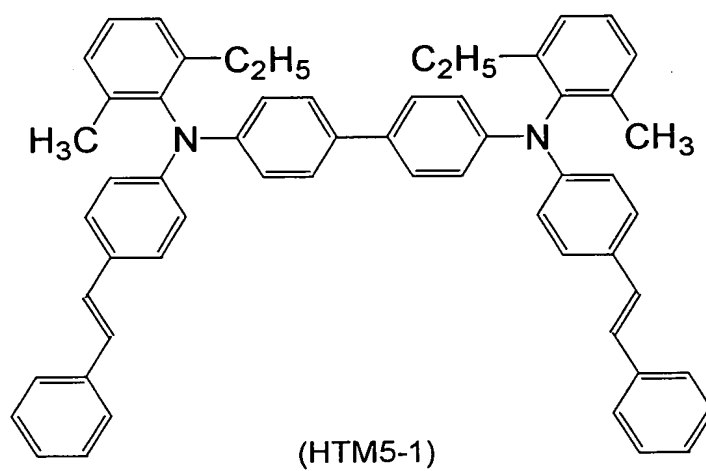
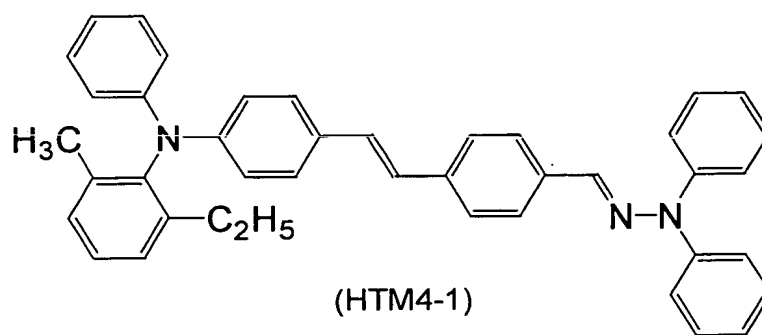


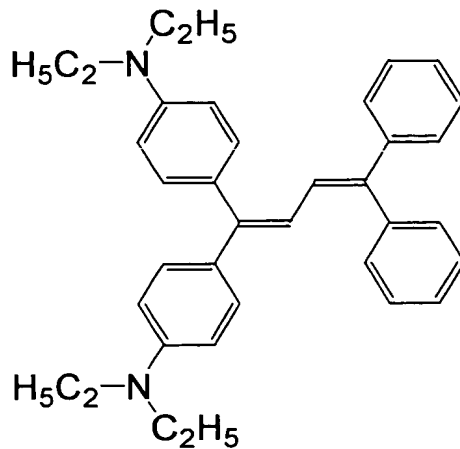
(HTM1-2)

10



(HTM3-1)





(HTM5-3)

With respect to the single-layer type electrophotosensitive material of Examples 17 to 22 and Comparative Examples 3 to 6,  
5 the evaluation for physical properties (measurement of sensitivity upon positive charging and wear amount) was carried out in the same manner as in Example 1. The results are shown in Table 3.



[Table 3]

[Single-layer type photosensitive material]

CGM: CGM1, ETM: ETM14-1

	Photosensitive layer-forming material		Evaluation of physical properties	
	Binder resin	HTM	Sensitivity upon positive charging (V)	Wear amount ( $\mu\text{m}$ )
Example 1	Resin-1	HTM1-1	136	1.09
Example 17	Resin-1	HTM1-2	135	1.10
Example 18	Resin-1	HTM3-1	146	1.12
Example 19	Resin-1	HTM4-1	147	1.02
Example 20	Resin-1	HTM5-1	142	1.19
Example 21	Resin-1	HTM5-2	293	1.18
Example 22	Resin-1	HTM5-3	261	1.19
Comparative Example 3	Resin-4	HTM5-2	280	1.62
Comparative Example 4	Resin-4	HTM5-3	245	1.60
Comparative Example 5	Resin-5	HTM5-2	277	1.35
Comparative Example 6	Resin-5	HTM5-3	244	1.39

As is apparent from Table 3, the electrophotosensitive materials of all Examples were excellent in sensitivity and durability (wear resistance). To the contrary, the electrophotosensitive materials of all Comparative Examples exhibited large wear amount. Therefore, a difference in wear resistance between the Examples and Comparative Examples was noticeable.

#### 10 Examples 23 to 26

In the same manner as in Example 1, except that compounds

shown in Table 4 were used as the electric charge generating material in place of the compound represented by the formula (CGM1), single-layer type electrophotosensitive materials were produced.

The electric charge generating material (titanyl  
5 phthalocyanine) represented by the formula (CGM2) is classified into a so-called Y type compound (CGM2 (Y)) and a so-called  $\alpha$  type compound (CGM2 ( $\alpha$ )) according to its crystal structure. Y type titanyl phthalocyanine was used in Example 23, while  $\alpha$  type titanyl phthalocyanine was used in Example 24. In Example 23, 3.5 parts  
10 by weight of CGM2 (Y) and 3.5 parts by weight of an azo pigment (C.I. Pigment 16) represented by the formula (Pig 1) were incorporated.

With respect to the single-layer type electrophotosensitive materials of Examples 23 to 26, the evaluation for physical  
15 properties (measurement of sensitivity upon positive charging and amount) was carried out in the same manner as in Example 1. The results are shown in Table 4.

[Table 4]

[Single-layer type photosensitive material]

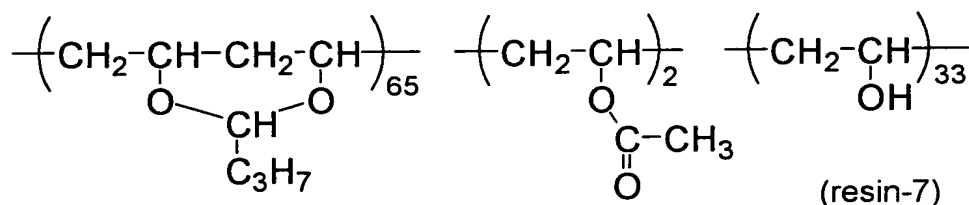
HTM: HTM1-1, ETM: ETM14-1

	Photosensitive layer-forming material		Evaluation of physical properties	
	Binder resin	CGM	Sensitivity upon positive charging (V)	Wear amount (μm)
Example 1	Resin-1	CGM1	136	1.09
Example 23	Resin-1	CGM2 (Y)	105	1.11
Example 24	Resin-1	CGM2 (α)	110	1.07
Example 25	Resin-1	CGM3	112	1.09
Example 26	Resin-1	CGM4	129	1.11

As is apparent from Table 4, the electrophotosensitive materials of all Examples were excellent in sensitivity and durability (wear resistance).

## Example 27

1 Part by weight of Y type titanyl phthalocyanine (CGM2 (Y)) and 1 part by weight of a polyallylate represented by the following formula (resin-7) were added in 48 parts by weight of a solvent (diacetone alcohol) and then dissolved and dispersed using an ultrasonic disperser to obtain a coating solution for formation of an electric charge generating layer.



70 Parts by weight of the hole transferring material (HTM1-1), 0.1 parts by weight of the leveling agent (aforementioned "KF-96-50CS") and 100 parts by weight of the binder resin (resin-1) were added in 550 parts by weight of a solvent (tetrahydrofuran) and then dissolved and dispersed using an ultrasonic disperser to obtain a coating solution for formation of an electric charge transferring layer.

First, the coating solution for formation of an electric charge generating layer was applied on an aluminum substrate by a dip coating method and then dried at 50°C for 30 minutes to form a 0.2  $\mu\text{m}$  thick electric charge generating layer. On the surface thereof, the coating solution for formation of an electric charge transferring layer was applied using a silicone blade and then dried at 110°C for 45 minutes to form a 30  $\mu\text{m}$  thick electric charge generating layer, and thus a multi-layer type electrophotosensitive material (negative charging type) was obtained.

Examples 28 to 29 and Comparative Example 7 to 9

In the same manner as in Example 27, except that a polyallylate (resin-2) was used as the binder resin in place of the binder resin (resin-1) in Example 28, a polyallylate (resin-3) was used in Example 29, a polyallylate (resin-4) was used in Comparative Example 7, and a polyallylate (resin-5) was used in Comparative Example 8, multi-layer type electrophotosensitive materials were produced.

In Comparative Example 9, a multi-layer type electrophotosensitive material was produced in the same manner as in Example 27, except that a polyvinyl butyral resin (resin-7) was used in place of the binder resin (resin-1) of the coating solution for formation of an electric charge transferring layer. (Evaluation of physical properties)

With respect to the single-layer type electrophotosensitive materials of Examples 27 to 29 and Comparative Examples 7 to 9, the following tests for evaluation of physical properties (3) and (2) were carried out.

(3) Measurement of sensitivity upon negative charging

An electrophotosensitive material was mounted to an electrostatic copying machine [modified type machine of aforementioned "KM-5530"] and, after charging the surface at -800 V and exposing the surface to red semiconductor laser light having a wavelength of 780 nm, a surface potential (bright potential) was measured.

The value of the surface potential upon exposure may be -90 V or higher.

The results of the evaluation of physical properties with respect to Examples 27 to 29 and Comparative Examples 7 to 9 are shown in Table 5.

[Table 5]

[Multi-layer type photosensitive material]

HTM: HTM1-1

	Photosensitive layer-forming material		Evaluation of physical properties	
	Binder resin	CGM	Sensitivity upon negative charging (V)	Wear amount ( $\mu\text{m}$ )
Example 27	Resin-7, Resin-1*	CGM2 (Y)	- 59	1.02
Example 28	Resin-2	CGM2 (Y)	- 63	1.14
Example 29	Resin-3	CGM2 (Y)	- 64	1.04
Comparative Example 7	Resin-4	CGM2 (Y)	- 55	1.49
Comparative Example 8	Resin-5	CGM2 (Y)	- 56	1.22
Comparative Example 9	Resin-7*	CGM2 (Y)	-155	6.22

5 \*: As the binder resin of Example 27, "resin-7" was used in the electric charge generating layer, while "resin-1" was used in the electric charge transferring layer as an outermost layer. In Comparative Example 9, "resin-7" was used as the binder resin in the electric charge generating layer and the electric charge transferring layer.

10 As is apparent from Table 5, the electrophotosensitive materials of both Examples and Comparative Examples were excellent in sensitivity. With respect to the durability (wear resistance) of the photosensitive layer, the electrophotosensitive materials of the Comparative Examples exhibited large wear amount, while the electrophotosensitive materials of the Examples exhibited very small wear amount. Therefore, a difference in wear resistance

between them was noticeable.

Examples 30 to 35 and Comparative Examples 10 to 13

5 In Examples 30 to 35, multi-layer type electrophotosensitive materials were produced in the same manner as in Example 27, except that compounds shown in Table 6 were used as the hole transferring material in place of the compound represented by the formula (HTM1-1).

10 In Comparative Examples 10 to 13, multi-layer type electrophotosensitive materials were produced in the same manner as in Example 27, except that compounds represented by the formulas (HTM5-2) or (HTM5-3) were used as the hole transferring material and polyallylate (resin-4) or a polycarbonate (resin-5) was used as the binder resin.

15 With respect to the multi-layer type electrophotosensitive materials of Examples 30 to 35 and Comparative Examples 10 to 13, the evaluation for physical properties (measurement of sensitivity upon negative charging and wear amount) was carried out in the same manner as in Example 27. The results are shown in Table 6.

[Table 6]

[Multi-layer type photosensitive material]

CGM: CGM2 (Y)

	Photosensitive layer-forming material		Evaluation of physical properties	
	Binder resin	HTM	Sensitivity upon negative charging (V)	Wear amount ( $\mu\text{m}$ )
Example 27	Resin-1	HTM1-1	-59	1.02
Example 30	Resin-1	HTM1-2	-62	0.95
Example 31	Resin-1	HTM3-1	-64	1.03
Example 32	Resin-1	HTM4-1	-66	1.05
Example 33	Resin-1	HTM5-1	-67	1.07
Example 34	Resin-1	HTM5-2	-93	1.15
Example 35	Resin-1	HTM5-3	-93	1.17
Comparative Example 10	Resin-4	HTM5-2	-88	1.49
Comparative Example 11	Resin-4	HTM5-3	-89	1.55
Comparative Example 12	Resin-5	HTM5-2	-92	1.23
Comparative Example 13	Resin-5	HTM5-3	-87	1.30

As is apparent from Table 6, the electrophotosensitive materials of all Examples were excellent in sensitivity and durability (wear resistance). To the contrary, the electrophotosensitive materials of all Comparative Examples exhibits large wear amount. Therefore, a difference in wear resistance between the Comparative Examples and the Examples was noticeable.

10 Examples 36 and 37



In the same manner as in Example 27, except that compounds shown in Table 7 were used as the electric charge generating material in place of the compound represented by the formula (CGM2 (Y)), multi-layer type electrophotosensitive materials were produced.

5 In Example 36,  $\alpha$  type titanyl phthalocyanine was used.

With respect to the multi-layer type electrophotosensitive materials of Examples 36 and 37, the evaluation for physical properties (measurement of sensitivity upon negative charging and wear amount) was carried out in the same manner as in Example 27.

10 The results are shown in Table 7.

[Table 7]

[Multi-layer type photosensitive material]

HTM: HTM1-1

	Photosensitive layer-forming material		Evaluation of physical properties	
	Binder resin	CGM	Sensitivity upon negative charging (V)	wear amount ( $\mu\text{m}$ )
Example 27	Resin-1	CGM2 (Y)	-59	1.02
Example 36	Resin-1	CGM2 ( $\alpha$ )	-80	1.02
Example 37	Resin-1	CGM3	-71	1.00

As is apparent from Table 7, the electrophotosensitive materials of all Examples were excellent in sensitivity and durability (wear resistance).

Comparative Examples 14 to 16

In the same manner as in Example 1 in case of Comparative

Example 9, Example 17 in case of Comparative Example 10, or Example 21 in case of Comparative Example 11, except that the polyallylate resin-6) obtained in Comparative Synthesis Example 2 was used as the binder resin in place of the polyallylate (resin-1),  
5 single-layer type electrophotosensitive materials were produced.  
(Evaluation of physical properties)

With respect to the single-layer type electrophotosensitive material of Examples 1, 17 and 21, and Comparatives Example 14 to 16, a test of evaluation for the following physical properties  
10 (i) and (ii) was carried out.

(i) Measurement of change in charge amount after exposure to NO<sub>x</sub> gas

Each of electrophotosensitive materials was mounted to an electrostatic copying machine (modified type machine of an  
15 electrostatic copying machine manufactured by KYOCERA MITA CORPORATION under the trade name of "Creage7325") and was charged while setting a grid voltage so that a surface potential becomes +800 V. Then, each of electrophotosensitive materials of the respective Examples and Comparative Examples to an NO<sub>x</sub> gas (24  
20 ppm) atmosphere for 50 hours and the surface potential under the same conditions of the grid voltage set before exposure was measured. Furthermore, a change in surface potential (v) before and after exposure to the NO<sub>x</sub> gas and the NO<sub>x</sub> resistance of the electrophotosensitive material was evaluated. For example, if  
25 the surface potential before exposure to the NO<sub>x</sub> gas is 800 V and

the surface potential after exposure is 690 V, the change is -110 V. The change in surface potential before and after exposure to the NO<sub>x</sub> gas may be -150 V or lower (a decrease in surface potential after exposure may be lower than 150 V). When the change exceeds  
5 -150 V (the change decreases after it exceeds -150 V after exposure), it is considered that the electrophotosensitive material is inferior in NO<sub>x</sub> resistance.

(ii) Change in properties of coating solution after exposure to NO<sub>x</sub> gas

10 The coating solutions for formation of the photosensitive layer prepared in Examples 1, 17 and 21, and Comparative Examples 14 to 16 were exposed to an NO<sub>x</sub> gas (24 ppm) atmosphere for 50 hours and, after 3 days have passed since the beginning of the exposure, properties of the coating solution were visually  
15 observed.

The results of the evaluation for physical properties with respect to Examples 1, 17 and 21, and Comparative Examples 14 to 16 are shown in Table 8.

[Table 8]

[Single-layer type photosensitive material]  
ETM: ETM14-1

	Photosensitive layer-forming material			Evaluation of physical properties	
	Binder resin	CGM	HTM	Change in charge amount after exposure	After 3 days
Example 1	Resin-1	CGM1	HTM 1-1	-51 V	no change
Example 17	Resin-1	CGM1	HTM 1-2	-33 V	no change
Example 21	Resin-1	CGM2 (Y)	HTM 1-1	-29 V	no change
Comparative Example 14	Resin-6	CGM1	HTM 1-1	-92 V	gelled
Comparative Example 15	Resin-6	CGM1	HTM 1-2	-75 V	gelled
Comparative Example 16	Resin-6	CGM2 (Y)	HTM 1-1	-61 V	gelled

As is apparent from Table 8, in the electrophotosensitive materials of the Examples, a change in charge amount after exposure was suppressed and no change in physical properties of the coating solution for formation of a photosensitive layer was observed. To the contrary, in the electrophotosensitive materials of the Comparative Examples, a change in charge amount after exposure was large and, moreover, the coating solution for formation of a photosensitive layer was gelled and large change in physical properties was observed. Therefore, a difference between the Examples and the Comparative Examples was noticeable.